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K. Matyjaszewski

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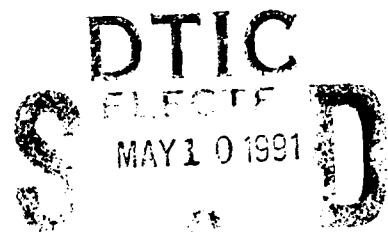
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Synthesis, modifications and characterization of various homopolysilanes and copolysilanes is reviewed with the main emphasis on the modification route and reductive coupling with various reducing agents and under various conditions.

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Polysilanes
Synthesis, Modification, and Properties

Krzysztof Matyjaszewski
Department of Chemistry, Carnegie Mellon University
4400 Fifth Avenue, Pittsburgh PA 15213

Introduction

Polysilanes are polymers with a linear Si-Si catenation in the main chain and with two organic substituents at each silicon atom. They have interesting physical and chemical properties and are of a potential commercial importance[1,2,3]. Poor compatibility of inorganic and organic segments provides morphologies with clear mesophases[4]. Photosensitivity of polysilanes leads to applications in microlithography[2,5]. Strong delocalization of electrons in the backbone provides materials with extremely interesting electronic properties: semiconductors, photoconductors, and nonlinear optical materials [1,2,6,7,8]. However, the synthetic aspect of polysilanes is not yet developed to the level corresponding to their physicochemical characterization. First, and still the most common preparative technique is based on the reductive coupling of disubstituted dichlorosilanes with alkali metals[9,10]. The polymodality of the obtained polymers limits some characterization techniques and also disables some applications[1,2]. The dehydrogenative coupling in the presence of transition metals usually provides low molecular weight materials[11,12]. There are two other routes to polysilanes based on the anionic polymerization of "masked disilenes"[13] and on the ring-opening polymerization[14]. These techniques may provide additional control of the microstructure of the nonsymmetrically substituted systems. In this paper some of our recent activities in the synthesis and characterization of polysilanes will be discussed. These include mechanistic studies of the sonochemical reductive coupling process, ring opening polymerization, and reactions on polysilanes, i.e. modification and grafting, as well as characterization of some copolysilanes.

Sonochemical Reductive Coupling Process

Polymerization of disubstituted dichlorosilanes with alkali metals via reductive coupling has a strong character of a chain (not a step) process. Molecular weights are very high at low conversions and independent of the [Mt]/[Si-Cl] ratio. Several intermediates such as silylene, radicals, and anions have been proposed as potential chain carriers.

We have demonstrated before that under sonochemical conditions (ambient temperature) polymerization has mostly ionic character, although the intermediate radicals coud be trapped as a short living species on the pathway from polymers terminated with ...-SiR_2-Cl to ...-SiR_2^-, Mt^+ [14,15,16]. The former participates in two one electron transfer processes, whereas the latter reacts with a monomer in the nucleophilic substitution process. The exact nature of the Si-Mt bond is still obscure and, under some conditions, it may have a covalent character.

In toluene, using sodium as a reducing agent, monomers with aryl groups react much faster than dialkylsubstituted dichlorosilanes[17]. The latters require elevated temperatures (above 80 °C), although they react readily with Na/K and K. However, phenylmethyldichlorosilane does not react with potassium within 2 hours under similar conditions. This apparent discrepancy has been solved by the analysis of the product of the reaction of phenylmethyldichlorosilane with K at longer reaction times. The resulting polymer ($M_n \approx 2,000$) is not a polysilane. It does not absorb above 300 nm and it contains a large amount of toluene moieties, in contrast to any other polysilanes. GC/MS analysis of the first products formed in

this reaction indicates the presence of Cl-SiMePh-PhMe species, formed via reaction of a monomeric radical with solvent. This result confirms the chain nature of the polymerization in which an electron transfer to a polymer chain occurs much faster than to the monomer. Of course, an electron transfer to phenylmethyldichlorosilane from potassium is much faster than from sodium, but initiation is still a few orders of magnitude slower than propagation. Moreover, an electron transfer from potassium may occur from a much longer distance than from sodium (in a way analoguous to Grignard reagent formation)[18]. Therefore, the monomeric radicals may be separated by two or three solvent molecules from the metal surface and, instead of the coupling process or the second electron transfer, they react with toluene or diffuse to the bulk solvent. Reaction of silyl radicals with toluene is very fast ($k=1.2 \times 10^6$ $\underline{M}^{-1}s^{-1}$)[19].

Reductive coupling at ambient temperatures in the presence of ultrasound leads to monomodal polymers with relatively narrow molecular weight distributions (M_w/M_n from 1.2 to 1.5) and relatively high molecular weights (M_n from 50,000 to 100,000)[17]. There are two phenomena responsible for the more selective polymerization. First, lower polymerization temperature and continuous removal of the sodium chloride from the sodium surface suppresses formation of the low molecular weight polymer (M_n from 2,000 to 10,000). This polymer might be formed via some side reactions (transfer or termination). Second, ultrasound mechanically degrades polysilanes with molecular weights above 50,000. This limit might be set by the chain entanglement and Si-Si bond energetics. Polysilanes prepared in separate experiments could also be selectively degraded. It seems that degradation in toluene in the presence of alkali metals is slightly accelerated, but no low molecular weight cyclooligosilanes are formed. On the other hand, in THF and diglyme (or in toluene in the presence of cryptands and potassium) polymer is completely degraded to cyclohexasilanes and cyclopentasilanes. The anionic intermediates have been observed spectroscopically in this degradation.

Copolymerization of various dialkylsubstituted dichlorosilanes by a reductive coupling process usually leads to statistical copolymers[20]. The copolymer composition usually corresponds to the monomer feed and the distribution of various triads, pentads, and heptads roughly corresponds to Bernoullian statistics.

Ring-Opening Polymerization

Reductive coupling of disubstituted dichlorosilanes with alkali metals is usually accompanied by the formation of cyclooligosilanes. Under some conditions, a polysilane can be easily degraded to the same cyclics. Thus, a polysilane can be considered as a kinetic product, whereas cyclic oligomers are true thermodynamic products. The majority of known cyclooligosilanes are thermodynamically stable and cannot be converted to linear polymers. Some potentially strained rings such as octaphenylcyclotetrasilanes can be prepared in high yield since the repulsive interactions between phenyl groups present at each silicon atom have a greater influence than the angular strain in the four membered ring. Additionally, low solubility and high melting point (mp. =323 °C) precludes polymerization of octaphenylcyclotetrasilanes at higher concentrations. We have discovered rapid and clean Si-Ar bond cleavage with trifluoromethanesulfonic acid[21]. Reaction of octaphenylcyclotetrasilanes with four equivalents of the acid leads to 1,2,3,4-tetra(trifluoromethanesulfonyloxy)-1,2,3 4-tetraphenylcyclotetrasilane. Subsequent reaction with either methylmagnesium iodide or methyl lithium yields four stereo isomers of 1,2,3,4-tetraphenyl-1,2,3,4-tetramethylcyclotetrasilane.

A Si-Si bond is quite labile in the presence of strong electrophiles and nucleophiles. Reaction with silyl anions leads to ring-opening and to the regeneration of silyl anions[22]. This is the propagation step. Silyl anions may also attack the Si-Si bonds in the polysilane chain and form macrocycles and strainless cyclooligosilanes. Rates of polymerization and degradation depend on solvent, temperature, and alkali metals. With 1 mol% of silyl potassium or butyl lithium initiator, only cyclooligosilanes have been found after less than 2 minutes at room temperature in pure THF. In benzene, with less than 3% THF, polymerization is completed after more than 1 hour. In mixtures of 60 % THF with benzene polymerization is completed within less than 2 minutes, but degradation starts after 1 hour. Polymers with molecular weights from 10,000 to 100,000 have been prepared via the anionic ring-opening polymerization of cyclotetrasilanes. This technique provides a pathway to various functional polymers and block copolymers.

Modification of Poly(phenylmethylsilylene)

The severe conditions of the reductive coupling process and the anionic process allow only alkyl and aryl substituents at silicon. There are only a few polysilanes known with substituents other than alkyl and aryl. However, the Si-Ph bond can be easily cleaved by strong protonic acids such as triflic acid. The rate of the dearylation is strongly influenced by the presence of an electron withdrawing group at the neighboring Si atoms. Model studies on dearylation of α,ω-diphenylpermethyloligosilanes with triflic acid indicate that the displacement of the first phenyl group is always faster than that of the second, even for pentasilanes:

$$\text{Ph-(SiMe}_2)_n\text{-Ph} \xrightarrow[k]{+\text{HOTf}} \text{Ph-(SiMe}_2)_n\text{-OTf} \xrightarrow[k']{+\text{HOTf}} \text{TfO-(SiMe}_2)_n\text{-OTf}$$
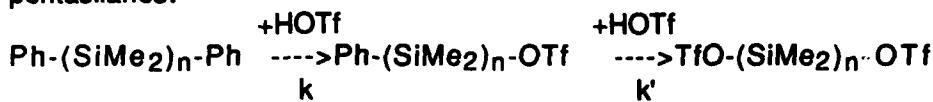
$k/k'=23, 13, 10, 7$ for $n=2, 3, 4, 5$

Apparently, the reactivity of the oligosilanes increases with the chain length in contrast to the electron density on the *ipso*-C atom which is attacked in the rate determining step. This indicates that the transition states rather than the ground states control reactivities of polysilanes.

The dearylation process applied to polysilanes containing phenyl substituents provides polymers with strong electrophilic silyl triflate moieties. Silyl triflates belong to the strongest known silylating reagents. They react with ketones 10^8 times faster than silyl chlorides do. They can react with any nucleophiles such as alcohols, amines, carbanions, organometallics, etc. This opens a new synthetic avenue towards various functional polysilanes[15,23]. The reactivity of silyl triflates is so high that they can initiate cationic polymerization of some alkenes and heterocyclics to form graft copolymers.

Solid State Transitions in Copolysilanes

The solid state of poly(di-n-alkyl)silylenes has been a subject of interest since the first discovery of intriguing UV-absorption properties by Miller et al [24]. Spincast films of polysilylenes generally show intense UV-absorptions. However, the absorption behavior of poly(di-n-alkyl)silylenes depends strongly upon the length of the side chains. Poly(di-n-pentyl)silylene (PDPS) shows an intense absorption band at 315 nm, which broadens upon heating to 100°C[25]. Contrary to these, poly(di n-hexyl)silylene (PDHS) shows a long wavelength absorption at 372 nm at room temperature, which transforms upon heating above 42°C to a less intense absorption at 316 nm. A similar behavior was reported for poly(di-n-alkyl)silylenes with longer side chains[26]. The thermochromism is usually thermally reversible. The different properties of PDPS and longer side chain homologues are attributed to changes in the backbone conformation of the polymers. The population of all-trans ordered segments present in the molecular backbone determines the length of the s-conjugated chromophores[27]. The investigation of copolymers with the isodimorphic[28] n-hexyl and n-pentyl units in various ratios was performed to give insight into the change from the 7/3 helical backbone conformation found for PDPS[29], to the all-trans backbone structure observed for longer side chains. The phase transitions of the copolymers were monitored by differential scanning calorimetry (DSC) as well as ^{29}Si-MAS solid state NMR and temperature dependent solid state UV-spectroscopy. Transition temperatures, UV-thermochromism and UV-absorption maxima can be controlled by copolymerizing isodimorphic n-pentyl-units. Defects introduced stepwise into the highly regular structure of poly(di-n-hexyl)silylene apparently lead to a decrease of the crystallinity, but for copolymers containing of up to 20% n-pentyl substituents, a predominantly all-trans structure is maintained. However, the blueshifted UV-absorptions reflect the loss of intramolecular order, resulting in backbone kinks and interruption of the conjugated s-chromophores. The decrease of the disordering temperature mirrors the loss of intermolecular order of the stiff molecules. In the disordered high temperature phase all copolymers seem to have a similar mesophase structure, with conformational disorder of the backbone and rotational motions of the side chains. A similar behavior has been observed for other inorganic-organic hybrid polymers[30]. As more n-pentyl side chains are incorporated, the packing of the all-trans rods becomes increasingly inefficient and short all-trans segments cannot sufficiently interact to preserve the planar backbone structure. Thus, a helical structure is adopted by the 50/50 co-PD(HS/PS). This polymer presents an energetic dilemma, similar as in the case of the atactic, asymmetrically substituted poly(n-hexyl n-pentyl) silylene[31].

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